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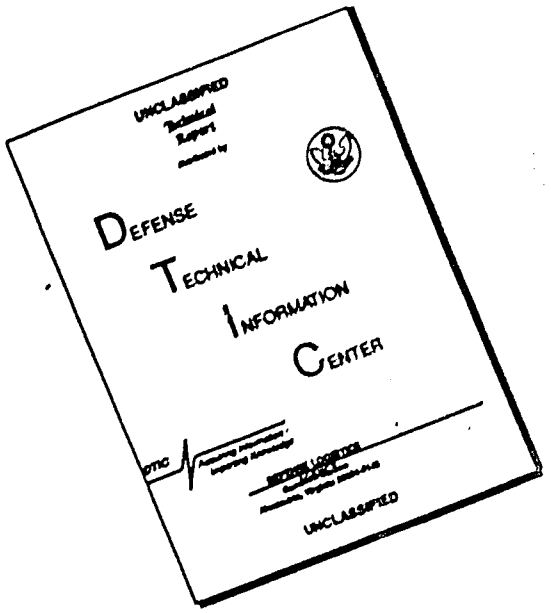

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THE UNIVERSITY OF WESTERN ONTARIO

DEPARTMENT OF PHYSICS

MOLECULAR EXCITATION GROUP

TRANSITION PROBABILITIES OF MOLECULAR BAND SYSTEMS

XXI Numerical Solution of the Schrodinger Wave Equation

by

W. R. JARMAIN

NOVEMBER 15, 1961

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SCIENTIFIC REPORT NO. 9

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ABSTRACT

Tests have been made of the Runge-Kutta and (especially) Numerov methods of solving the reduced Schrödinger wave equation for a tabulated Morse potential. This is preliminary to numerical solution of the equation for a Klein-Dunham potential.

Normalized wave functions for N_2, $B^3\Pi$, of orders 0 and 5, given at an interval of 0.01Å in internuclear separation, agree closely with those obtained analytically.

A criterion for goodness of wave functions generated numerically, depending on observed rotational constants, is described.

1. INTRODUCTION

This report describes the first phase of a project to solve the reduced Schrödinger wave equation numerically, given a tabulated Klein-Dunham potential energy function (Klein 1932, Dunham 1932, Jarmain 1960, 1961). The 'true' potential, as is well known, is not available ir closed form.

For certain diatomic molecular transitions, Morse vibrational wave functions are inadequate for the calculation of Franck-Condon factors and other parameters. Therefore we wish to determine how large the discrepancies are that sometimes exist between Franck-Condon factors based on a Morse potential, and those based on a more accurate Klein-Dunham function.

Such factors are often useful in their own right in predicting approximate relative intensities of molecular bands, and of course have been used extensively in conjunction with good measured intensities to yield the shape of the electronic transition moment (see e.g. Hebert and Nicholls 1962).

The present summary deals only with the numerical solution of the wave equation for a tabulated Morse potential. It was considered prudent first to verify that correct Morse wave functions could be so generated, especially when these were available for checking from earlier analytic work.

2. Solution of the Differential Equation

Neglecting rotation, the reduced Schrödinger equation satisfied by a vibrational wave function $\psi_v(r)$, with v the vibrational quantum number, is:

$$\frac{d^2\psi_v}{dr^2} + \frac{8\pi^2\mu}{h^2}\left[E_v - U(r)\right]\psi_v = 0 \qquad (1)$$

where r is internuclear separation, μ is the reduced mass of the molecule, E_v is the appropriate eigenvalue, and $U(r)$ is the vibrational potential energy function.

Tests of the method described below were carried out on N_2, $B^3\Pi$ for the following reasons. Firstly, ordinates of Morse wave functions up to order 12 had been calculated previously for this state from formulae (Jarmain and Nicholls 1952, 1960). Secondly, there is good agreement (mostly less than 1% deviation) between the tabulated Morse and Klein energies at specific values of r. Finally, if a theoretical rotational constant α_e, $\left[B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right)\right]$, is determined from Pekeris' (1934) relation

$$\alpha_e = \frac{6 B_e^2}{\omega_e} \left[\sqrt{\frac{\omega_e x_e}{B_e}} - 1\right] \qquad (2)$$

it agrees with the observed α_e to about 0.5%. Thus, anticipating the use of a Klein-Dunham potential to obtain wave functions, one would expect fairly good point by point agreement with corresponding Morse functions. This would provide a preliminary check on the validity of the procedure used to start the Klein-Dunham solution. A later report will discuss that procedure.

Solutions were first obtained using a Runge-Kutta fourth order process as adapted for digital computers by Gill (1951). This choice was made because it was available as a subroutine in the U.W.O. Computing Centre Library, because it is known to be very stable and requires

knowledge of only one point and a slope at that point for starting. These values were determined from analytic Morse expressions, on the extreme left side of the wave function beyond which point ordinates are so small that they contribute nothing significant, for four figure accuracy, to an overlap integral involving a wave function of another electronic state. Integration then proceeded from left to right.

As anticipated, this method was effective but relatively slow. It did, however, indicate sensitivity of the curve to choice of eigenvalue and also a suitable sub-interval size for integration. For each of the two orders tested, a start was made with the experimental eigenvalue, but minor adjustment in it was necessary to keep ordinates numerically small over a reasonable interval on the right hand side. At best, wave functions remained unbounded at $r = \infty$, but were simply cut off in the region of smallest ordinates. Not surprisingly, the subinterval had to be diminished as the order of the wave function increased.

The Runge-Kutta-Gill routine was then abandoned in favour of a formulation due to Numerov (1933) a partial derivation of which follows. Taken from central difference theory, equation (3) (Hartree 1958) relates the second difference of a function to its second derivative and differences of the latter, namely,

$$\delta^2\psi_0 = (\delta r)^2 \left\{ \psi_0'' + \frac{1}{12}\,\delta^2\psi_0'' - \frac{1}{240}\,\delta^4\psi_0'' \right\} + 0\,(\delta r)^8 \qquad (3)$$

Equation (1) to be solved is of the form

$$\psi'' = F(r)\,\psi \qquad (4)$$

Neglecting the fourth difference in (3), we have

$$\delta^2\psi_0 = (\delta r)^2 \left[\psi_0'' + \frac{1}{12}\delta^2\psi_0''\right] \tag{5}$$

It is also true that

$$\delta^2\psi_0 = \psi_1 - 2\psi_0 + \psi_{-1} \tag{6}$$

where the subscripts refer to consecutive values of ψ. Again, by virtue of (4)

$$\psi_0'' = F_0\,\psi_0$$

$$\delta^2\psi_0'' = F_1\,\psi_1 - 2F_0\,\psi_0 + F_{-1}\,\psi_{-1} \tag{7}$$

Therefore, combining equations (5), (6) and (7),

$$\left[1 - \frac{1}{12}(\delta r)^2 F_1\right]\psi_1 - 2\left[1 - \frac{1}{12}(\delta r)^2 F_0\right]\psi_0 + \left[1 - \frac{1}{12}(\delta r)^2 F_{-1}\right]\psi_{-1} = (\delta r)^2 F_0\psi_0 \tag{8}$$

Finally, a formula for ψ_1 in terms of ψ_0 and ψ_{-1} is

$$\left[1 - \frac{1}{12}(\delta r)^2 F_1\right]\psi_1 = \left[2 + \frac{5}{6}(\delta r)^2 F_0\right]\psi_0 - \left[1 - \frac{1}{12}(\delta r)^2 F_{-1}\right]\psi_{-1} \tag{9}$$

Thus, Numerov's equation (9) generates the functional value ψ_1 if two starting values ψ_0 and ψ_{-1} are provided, and of course the calculated ψ_1 is needed together with ψ_0, to produce ψ_2 at the next step, and so on. The technique is fast and sufficiently accurate for the purpose, providing a suitably fine subdivision is used. As mentioned before, the observed eigenvalue does not give a wave function that is well behaved on the right hand side. This is probably mainly due to the approximate nature of the procedure.

3. RESULTS

Morse wave functions of order 0, 5 and 10 have been constructed using

TABLE I

MORSE WAVE FUNCTION

N_2 $B^3\Pi$ v = 0

r(A)	Analytic	Numerical	r(A)	Analytic	Numerical
1.02	1.011x10	1.011x10	1.23	$3.149x10^4$	$3.149x10^4$
1.03	2.410x10	2.410x10	1.24	$2.944x10^4$	$2.944x10^4$
1.04	5.430x10	5.430x10	1.25	$2.662x10^4$	$*2.661x10^4$
1.05	$1.158x10^2$	$1.158x10^2$	1.26	$2.328x10^4$	$2.328x10^4$
1.06	$2.340x10^2$	$2.340x10^2$	1.27	$1.973x10^4$	$1.973x10^4$
1.07	$4.488x10^2$	$4.488x10^2$	1.28	$1.620x10^4$	$1.620x10^4$
1.08	$8.179x10^2$	$*8.180x10^2$	1.29	$1.290x10^4$	$1.290x10^4$
1.09	$1.418x10^3$	$1.418x10^3$	1.30	$9.975x10^3$	$9.975x10^3$
1.10	$2.342x10^3$	$*2.343x10^3$	1.31	$7.491x10^3$	$7.491x10^3$
1.11	$3.690x10^3$	$3.690x10^3$	1.32	$5.469x10^3$	$5.469x10^3$
1.12	$5.549x10^3$	$5.549x10^3$	1.33	$3.883x10^3$	$3.883x10^3$
1.13	$7.977x10^3$	$7.977x10^3$	1.34	$2.684x10^3$	$2.684x10^3$
1.14	$1.097x10^4$	$1.097x10^4$	1.35	$1.807x10^3$	$1.807x10^3$
1.15	$1.446x10^4$	$1.446x10^4$	1.36	$1.186x10^3$	$1.186x10^3$
1.16	$1.827x10^4$	$1.827x10^4$	1.37	$7.586x10^2$	$7.586x10^2$
1.17	$2.215x10^4$	$2.215x10^4$	1.38	$4.737x10^2$	$*4.736x10^2$
1.18	$2.582x10^4$	$2.582x10^4$	1.39	$2.888x10^2$	$*2.885x10^2$
1.19	$2.893x10^4$	$2.893x10^4$	1.40	$1.720x10^2$	$*1.716x10^2$
1.20	$3.122x10^4$	$3.122x10^4$	1.41	$1.002x10^2$	*9.941x10
1.21	$3.245x10^4$	$3.245x10^4$	1.42	5.704x10	*5.577x10
1.22	$3.254x10^4$	$3.254x10^4$			

Asterisks indicate where analytic and numerical values differ.

TABLE II

MORSE WAVE FUNCTION

N_2 $B^3\Pi$ v = 5

r(A)	Analytic	Numerical	r(A)	Analytic	Numerical
1.01	5.734×10^{2}	$*5.735\times10^{2}$	1.29	-1.600×10^{3}	-1.600×10^{3}
1.02	1.187×10^{3}	$*1.188\times10^{3}$	1.30	8.854×10^{3}	$*8.855\times10^{3}$
1.03	2.285×10^{3}	$*2.286\times10^{3}$	1.31	1.677×10^{4}	1.677×10^{4}
1.04	4.083×10^{3}	4.083×10^{3}	1.32	2.011×10^{4}	2.011×10^{4}
1.05	6.760×10^{3}	6.760×10^{3}	1.33	1.831×10^{4}	1.831×10^{4}
1.06	1.034×10^{4}	1.034×10^{4}	1.34	1.215×10^{4}	1.215×10^{4}
1.07	1.455×10^{4}	1.455×10^{4}	1.35	3.308×10^{3}	3.308×10^{3}
1.08	1.869×10^{4}	1.869×10^{4}	1.36	-6.216×10^{3}	-6.216×10^{3}
1.09	2.167×10^{4}	2.167×10^{4}	1.37	-1.468×10^{4}	-1.468×10^{4}
1.10	2.220×10^{4}	2.220×10^{4}	1.38	-2.091×10^{4}	-2.091×10^{4}
1.11	1.921×10^{4}	1.921×10^{4}	1.39	-2.442×10^{4}	-2.442×10^{4}
1.12	1.244×10^{4}	1.244×10^{4}	1.40	-2.530×10^{4}	-2.530×10^{4}
1.13	2.802×10^{3}	2.802×10^{3}	1.41	-2.406×10^{4}	-2.406×10^{4}
1.14	-7.524×10^{3}	-7.524×10^{3}	1.42	-2.139×10^{4}	-2.139×10^{4}
1.15	-1.564×10^{4}	-1.564×10^{4}	1.43	-1.797×10^{4}	-1.797×10^{4}
1.16	-1.887×10^{4}	-1.887×10^{4}	1.44	-1.438×10^{4}	-1.438×10^{4}
1.17	-1.592×10^{4}	-1.592×10^{4}	1.45	-1.102×10^{4}	-1.102×10^{4}
1.18	-7.539×10^{3}	-7.539×10^{3}	1.46	-8.114×10^{3}	-8.114×10^{3}
1.19	3.481×10^{3}	3.481×10^{3}	1.47	-5.765×10^{3}	-5.765×10^{3}
1.20	1.324×10^{4}	1.324×10^{4}	1.48	-3.961×10^{3}	-3.961×10^{3}
1.21	1.817×10^{4}	1.817×10^{4}	1.49	-2.638×10^{3}	-2.638×10^{3}
1.22	1.645×10^{4}	1.645×10^{4}	1.50	-1.706×10^{3}	-1.706×10^{3}
1.23	8.723×10^{3}	8.723×10^{3}	1.51	-1.073×10^{3}	-1.073×10^{3}
1.24	-2.175×10^{3}	$*-2.176\times10^{3}$	1.52	-6.577×10^{2}	$*-6.576\times10^{2}$
1.25	-1.231×10^{4}	-1.231×10^{4}	1.53	-3.930×10^{2}	$*-3.929\times10^{2}$
1.26	-1.814×10^{4}	-1.814×10^{4}	1.54	-2.293×10^{2}	$*-2.290\times10^{2}$
1.27	-1.779×10^{4}	-1.779×10^{4}	1.55	-1.308×10^{2}	$*-1.302\times10^{2}$
1.28	-1.154×10^{4}	-1.154×10^{4}			

Asterisks indicate where analytic and numerical values differ.

an I.B.M. 650, with detailed results given for the first two. The tenth order is still under study, with indications that a sub-interval of less than 0.005A is needed. Intervals used for the others were 0.01A and 0.005A respectively.

Table I shows a comparison between normalized ordinates obtained analytically to four figures and those from the present method, for $v = 0$. The final eigenvalue was 863.44468 cm^{-1} compared with the observed 863.438 cm^{-1}. Starting values at 1.02A and 1.03A were 10.110 and 24.097 respectively, with r measured in cm. Table II gives a similar comparison for the fifth order, with eigenvalue of 9098.3955 cm^{-1} against the observed 9099.888 cm^{-1}. Starting values at 1.010A and 1.015A were 5.7332×10^2 and 8.3259×10^2 respectively. In general, agreement is perfect to four figures except on the extreme right.

A. B_v Test

It was felt from the beginning that as many checks as possible should be provided for the normalized Klein-Dunham wave functions eventually to be constructed numerically. Otherwise it would be unsafe to claim that these functions are necessarily an improvement on Morse. One test that is immediately available is of course orthogonality between wave functions of different order. A second one, which depends on observed rotational constants, was devised by Dr. P.A. Fraser.

According to Herzberg (1950), p. 106, it is plausible to use a mean value for the rotational constant B in the vibrational state considered, that is

$$B_v = \frac{h}{8\pi^2 c\mu}\left[\frac{1}{r^2}\right] \qquad (10)$$

where $\overline{\frac{1}{r^2}}$ is the mean value of $\frac{1}{r^2}$ during the vibration. See also Hylleraas (1936) for justification. But $\overline{\frac{1}{r^2}}$ is given as well by $\int_0^\infty \left[\frac{\psi_v(r)}{r}\right]^2 dr$, which can be evaluated numerically for any tabulated wave function over the significant range of r. Note that the Morse wave function is not zero at the origin, although extremely small, and therefore the integrand is infinitely great at the lower limit. In practice, however, we integrate no nearer to the origin then say 0.5A (more in this case), because ordinates are then trivially small. For purposes of the test, one can assume over the remaining interval a segment of the true wave function which will be of a high enough order of smallness (zero) at the origin to overcome the effect of r^{-2} in the integrand. Thus, comparison of the right hand side of equation (10) with the experimental B_v should give a good indication of the correctness of the wave function ψ_v.

Results of applying this test to the Morse functions above were $B_0 = 1.6290$ cm^{-1} compared with 1.6288 cm^{-1} observed, and $B_5 = 1.5362$ compared with 1.5368. The wave function of lower order is evidently more nearly correct on the basis of the above criterion. It is hoped that further tests can be developed as work continues.

5. FUTURE PROGRAM

The next report will deal with construction and testing of Klein-Dunham wave functions obtained by the present method for N_2, $B^3\Pi$ and possibly other molecular states. This work is already under way but subject to revision and therefore not ready for publication.

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